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- (71) Applicant (for all designated States except US): **COMPANHIA BRASILEIRA DE METALURGIA E MINERAÇÃO - CBMM** [BR/BR]; Rua Pequetita, 111, Vila Olímpia, 04552-902 São Paulo-SP (BR).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): **TAGUSAGAWA, Solon, Yasuhiko** [BR/BR]; Rua Engenheiro Afonso Bauer, 104, 05616-080 São Paulo - SP (BR).
- (74) Agent: **MOMSEN, LEONARDOS & CIA.**; Mr. Gustavo José F. Barbosa, Rua Teófilo Otoni 63, 10th floor, 20090-080 Rio de Janeiro RJ (BR).

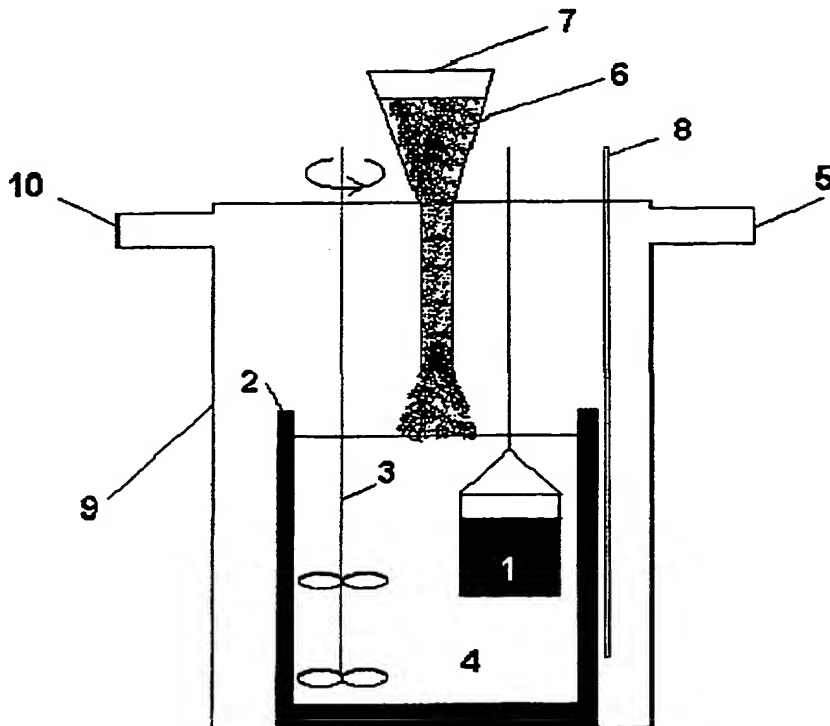
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(54) Title: A PROCESS FOR THE PRODUCTION OF NIOBIUM AND/OR TANTALUM POWDER WITH LARGE SURFACE AREA



(57) Abstract: The present invention refers to a process for production of a powder of niobium and/or tantalum having high purity, large specific surface area, controlled contents of oxygen and nitrogen, and a morphology that is adequate for use in the manufacture of capacitors, characterized by including one sole step of reduction of a controlled layer of niobium and/or tantalum oxide (Nb_xO_y , and/or Ta_xO_y , where $x = 1$ to 2 and $y = 1$ to 5) deliberately formed over particles of metallic niobium and/or tantalum and/or hydrides thereof of adequate purity, by alkali metals or earth alkali metals and/or hydrides thereof in a bath of molten salts followed by a step of dissolution of the salt in an aqueous solution for recovery of the niobium and/or tantalum powder. These particles produced using the said process have a small size, large surface area and a sponge-like morphology, being thereby adequate for the production of capacitors.

“A PROCESS FOR THE PRODUCTION OF NIOBIUM AND/OR TANTALUM POWDER WITH LARGE SURFACE AREA”.

The present invention refers to a process for the production of niobium and/or tantalum powder by means of reduction of a controlled layer of niobium and/or tantalum oxide (Nb_xO_y , and/or Ta_xO_y , where $x = 1$ to 2 and $y = 1$ to 5) deliberately formed over particles of metallic niobium and/or tantalum and/or hydrides thereof of high purity by a reaction metal dissolved in a solution of molten salts in a controlled atmosphere.

10

The reduction of oxides of niobium and/or other refractory metals by metals and/or hydrides of alkali metals or alkali earth metals is well known, as may be noted in Patents Nos. US 1,728,941, US 2,516,863, US 4,687,632, US 6,136,062, US 6,171,363, DE 19831280 and WO 00/15555.

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The main problem of the metallothermal reaction is its strongly exothermal and uncontrolled reaction, causing an excessive heating of the system and impairing the characteristics of the powder that is produced (increase in mean particle size and decrease of specific area).

20

One of the manners of controlling the reaction is to perform the reduction initially to a sub-oxide of niobium, such as described in some patents, since in this condition the exothermal characteristic of the reaction is less intense. The sub-oxide thus produced would then be reduced to metallic niobium, again with less intense exothermal behavior, producing a powder with the recommended characteristics. However, such procedure

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creates a need to conduct the process in two stages, requiring an increased consumption of energy and time. Furthermore, the possibility of contamination of the powder is increased due to the greater number of stages under high temperatures in contact with the oven atmosphere, with the reducing agent and with the container where the reaction takes place. Some patents mention the need to use forced cooling of the reactor and/or use of mechanical stirring devices, in order to decrease the exothermal effect of the reaction and to promote the dissipation of heat. One other form of reaction that is mentioned consists in the use of the alkali metal or earth metal in the form of vapor. The use of a vapor is justified to solve the problems that occur when the reducer is used in the liquid state. However, the use of this technique frequently entails a need to conduct subsequent deoxidizing steps, since one most always fails to achieve a full reduction in one sole step. Furthermore, although the vaporization of alkali metals or earth alkali metals is endothermic, the reduction of the niobium oxides through the use of these metals in the form of vapor is more exothermal than when they are used in liquid form. This is detrimental to the control of the reaction towards avoiding overheating.

The use of the technique of reduction in molten salts is cited for the production of niobium and/or other refractory metals, however employing other sources of niobium such as potassium fluoroniobate, using sodium as a reducing agent (US Patent No. 4,684,399), or reducing this same compound with sodium using as diluent a bath of molten salts comprised of KCl-KF or KCl-NaCl (WO 01/59166) and niobium pentachloride reduced by reaction metals dissolved in a solution of molten salts (US Patent No. 4,725,312 and WO 01/59166).

The process disclosed in US Patent No. 4,725,312 and WO 01/59166 proposes a process for the production of metals in powder form of groups IV-B and V-B of the Periodic Table of Elements (US Patent No. 4,725,312) by reducing the salts of those metals through the use of a bath of molten salts containing lithium as the reducing agent. A wide range of binary mixtures of salts is mentioned, among which there should be pointed out: LiCl-KCl, CsCl-LiCl, RbCl-LiBr and KBr-LiBr, LiCl-NaCl-CsCl, LiCl-NaCl-RbCl and LiCl-KCl-KF. In this process the bath of salts is kept at a temperature between 400 and 550°C. The quantity of lithium present in the bath of molten salts should at least be the stoichiometric amount required for the reduction of the chlorides of Nb, Ti and Nd, and these chlorides may be introduced in solid, liquid or gas form, this latter being preferred.

The patent application publications Nos. WO 01/82318 and WO 01/59166 mention the production of niobium powders by means of the reduction of K_2NbF_7 using sodium as the reducing agent added to a bath of molten salts (KCl-KF or KCl-NaCl).

The main advantages of the use of the method of reduction in molten salts are: a) the dissipation of the heat generated in the reaction occurs in the bath of salts thus avoiding localized overheating; b) it is possible to control the reducing potential of the reducing agent by means of the dissolution thereof in a molten salt; c) it is possible to continuously feed both the reducing agent and the raw material containing Nb and/or Ta to the salts bath and thereby to control the speed of reduction and therefore the generation of heat; d) avoiding direct contact between the reducing

agent and the source of Nb and/or Ta, decreasing the possibility of sintering and inadequate growth of the powder of Nb and/or Ta thus reduced; e) it is possible to stir the bath of salts, and therefore to allow control over the speed of the reaction increasing or decreasing the rate of dissolution both of the reducing agent and of the source of Nb and/or Ta in the molten salt; f) it is possible to control the reaction temperature by proper selection of a salt solution which melting temperature is compatible with the temperature at which it is desired to conduct the reaction; g) easy recovery of the powder of Nb and/or Ta thus produced, since it is merely necessary to dissolve the salt in an aqueous solution to recover the same; h) the oxides of alkali metals or earth alkali metals dissolve in the salt preventing the formation of barriers between the reagent and the reducing agent; i) it is not necessary to use the reducing agent in powdered or granulated form; j) it is possible to introduce a doping element – nitrogen in the Nb and/or the Ta, through the atmosphere of the oven that keeps the salt in the molten state, either by injecting N₂ gas into the bath of salts or by means of agents that carry the doping element and which may dissolve in the molten salt and k) it is possible to introduce a doping element – phosphorus in the Nb and/or the Ta, by means of agents that carry the doping element which may dissolve in the molten salt.

With this method, the oxide of niobium and/or tantalum may be reduced in a controlled manner with a strong reducing agent producing a power of high purity, with a sponge-like morphology, of low apparent density and large specific surface area. Additionally, since the raw material is a metallic niobium and/or tantalum powder and/or hydrides thereof of high purity and adequate size, that was previously oxidized in a controlled

manner to have an adequate layer of oxide, the thermal energy generated in the reduction of this layer of oxide is much less than that which would be generated to obtain the same particle if the raw material was to consist entirely in oxide. This lesser generation of energy facilitates the control of the process such that the possibility of contamination by gasses and other metals is significantly reduced, which may be evidenced by the low leakage current of the powder obtained using this process.

DETAILED DESCRIPTION OF THE INVENTION

10 The present invention comprises a process for the production of metallic powder of niobium and/or tantalum by means of metallothermal reduction in molten salts wherein the problems of overheating during the reduction, or of the need to conduct the process in more than one step, are eliminated.

15 With such procedure, it is possible to control and to dissipate the heat generated in the mixture due to the presence of the salts bath, to control the speed of the reaction, by controlling the feed rate of the reagents and avoiding direct contact of the reducing agent with the reagent. In addition to the thermal aspect, the reaction is more controlled due to the possibility of controlling the potential of the reducing agent, due to the same being diluted in the salt at the desired concentration. In this manner, the driving force for the reduction may be controlled, allowing increased control of the process. The use of a raw material in the form of a powder, 20 of adequate size, consisting basically in metallic niobium and/or tantalum and/or hydrides thereof, of high purity, previously oxidized in a controlled manner (hereinafter referred as "oxidized powder"), leads to a uniform

precipitation of the Nb and/or the Ta, with the aspect of a sponge, within the medium of liquid salt, producing an adequate distribution of particles without the formation of clusters of undesirable size.

5 The reducing agent is an alkali or earth alkali metal, preferably calcium or magnesium and/or a hydride of such metal. Nitrides of alkali metals or earth alkali metals may also be fed to the reactor constituting sources of N₂ for the produced niobium and/or tantalum.

10 The reduction occurs at temperatures between 300 and 1200° C, preferably between 500 and 1000° C in an inert atmosphere (argon or helium) or a reactive atmosphere containing, for example, nitrogen (N₂).

15 During the reduction, the salt may be subjected to mechanical stirring or to the injection of an inert or partially inert gas containing, for example, N₂. The molten salt may be comprised of mixtures of salts or of pure salts, such as fluorides and chlorides of Ca, Li, Ba, Mg, K and Na. The salts evidencing greater solubility of the reducing agent are preferred, such as CaCl₂ when employing calcium as reducing agent.

20 The reducing agent and the oxidized Nb and/or Ta powder may be continuously fed to the molten salt using devices that allow to control the feed rate of both. The temperature of the process may be kept constant by controlling the feed rate of the raw materials. The quantity of
25 reducing agent that is used should be at least the stoichiometric amount for the reduction of all the oxide of the oxidized powder of Nb and/or Ta that is fed. There may be employed a quantity up to 800% of the stoichiometric

amount. Such excess depends, among other parameters, on the quantity of salts bath.

Both the reducing agent and the "oxidized powder" may be added together with the salt bath to the reduction reactor prior to the melting step or may be fed separately or together to the salt bath upon the prior melting thereof. This feeding may be carried out continuously or otherwise. The quantity of reducing agent is substantially less in comparison to the reduction of particles of oxides, and depending on the oxygen content of the oxidized powder, the required quantity of reducing agent may be previously added to the salt bath.

Normally the following salts or mixtures thereof are employed to control the reaction: CaCl_2 , NaCl , KCl and MgCl_2 . The mixture of salts allows the reduction to occur at a lower temperature, allowing to obtain smaller particle sizes and larger surface areas. The quantity of salt or mixture of salts will have an effect on the control of the reaction temperature, the greater is the quantity of salt the easier it will be to control the temperature. The quantity of salt used may vary between 5 and 100g/g of oxidized powder fed.

The reaction may be carried out in stainless steel, nickel, tantalum or niobium reactors, depending on the degree of contamination that can be tolerated in the product obtained.

After the reaction, the resulting salt mixture containing metallic niobium and/or tantalum is dissolved in deionized water and is

subsequently filtered and leached with a solution containing HCl and which may also contain HF, HNO₃ and H₂SO₄. After the leaching the material is rinsed and dried.

5 The amount of water for solubilization of the salt varies between 10 and 100 liters for every 5 kg of salt. For the acid leaching step there are used 1 to 100 ml of solution for every gram of powder obtained from dissolution of the salt.

10 The control of the nitrogen content in the Nb and/or Ta may be effected by controlling the partial pressure of N₂ in the atmosphere of the oven, by an injection of N₂ gas or of mixtures of gasses containing N₂ into the molten salt, or yet, by the addition of N₂ carrier elements, such as nitrides soluble in the molten salt. A part of the nitrogen is dissolved in the
15 solution of salts allowing that nitride ions may be available to allow the solubilization of nitrogen in the particles of Nb and/or Ta. Similarly, it is possible to dope with phosphorus by adding phosphorus compounds soluble in the salt bath.

20 The particles of powder of Nb and/or Ta produced using the present process have a reduced size, have a large surface area and a sponge-like morphology, and are adequate for the production of capacitors.

 The reducing procedure consists in melting the salt initially in
25 a stainless steel, nickel, niobium or tantalum reactor, either or not in the presence of the oxidized powder, and of the reducing agent in an inert gas atmosphere. Before the heating of the reactor, the oven chamber should be

evacuated and then pressurized with the inert gas at pressures that may vary from 400 to 1200 torr. After the salt is molten, the temperature is stabilized between 30 and 150° C above the melting point of the salt or of the reducing metal, whichever has the higher melting point. From this moment on there is started the stirring process of the bath using a mechanical agitator or by means of injection of an inert or reactive gas (N₂ or a mixture of N₂ with an inert gas). If the reducing agent and/or the "oxidized powder" have not been previously added, there is initiated the addition of both or of one of them using an adequate system that allows to control the feed rate to the salt bath.

After having awaited the time required for reaction, the stirring is discontinued and the oven is turned off to allow the cooling of the salt containing metallic Nb and/or Ta.

The time required for the reduction will depend on the feed rate of the reducing agent or the oxidized powder, or yet of the quantity of powder and reducer fed together with the salt prior to the beginning of the reaction.

The feed rate of the oxidized powder is an important parameter for the control of the process, since it may control the localized generation of heat. However, as previously explained, this amount of heat is substantially less when compared to the use of oxide of Nb and/or Ta as source of Nb and/or Ta.

The reduction temperature may have an influence on the

surface area of the produced powder. Higher temperatures may lead to larger particles with lesser specific surfaces. Therefore, the selection of the mixture of salts is important with a view to lowering the temperature of the process.

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Stirring the salt is also important to avoid localized overheating and to disperse the oxidized powder, avoiding its segregation in the bath.

10 **BRIEF DESCRIPTION OF THE DRAWINGS**

The present invention is described with further detail in reference to the attached Figures, wherein identical numerals represent identical structures throughout the various drawings, and wherein:

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Figure 1 is a schematic drawing of a reactor for reduction of the oxidized powder;

Figure 2 depicts a detail of the support stem inside the crucible; and

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Figure 3 illustrates back-scattered electrons of the typical morphology of powders produced using the processes set forth herein.

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Figure 1 is a schematic drawing of the reactor used for the reduction in molten salts where the oxidized powder is continuously fed in a crucible containing a molten salt. In the same crucible that contains the salt, there is placed another container, submerged in the salt, containing the liquid alkali metal or earth alkali metal. The identifications of Figure 1 are:
1- Crucible containing the liquid alkali metal or earth alkali metal; 2-

Crucible containing the molten salt; 3- Stirring stem; 4- Molten salt; 5- Inert or reactive gas inlet; 6- "oxidized powder"; 7- Container with the "oxidized powder" contained therein; 8- Thermocouple; 9- Oven chamber and 10- Vacuum system outlet.

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In this system, the mechanical stirring may be substituted by stirring caused by injection of an inert or reactive gas.

After cooling of the reactor in an inert atmosphere, the produced material is dissolved in deionized water. The solution obtained in the dissolution of the salt is filtered, and is then leached in a solution containing HCl, HNO₃, H₂SO₄ and HF. The amount of leaching solution employed is 1 to 100 ml/g of filtered product, preferably 10 to 40 ml/g. After this leaching, there is performed a final rinsing with deionized water, filtration and subsequently, vacuum-drying.

15

According to the present invention, the powder of Nb and/or Ta obtained has contents of Mg and Ca below 500 ppm, sodium content below 50 ppm, oxygen content between 1,000 and 4,000 ppm/(m²/g), sum total of contents of Fe, Cr and Ni below 300 ppm and a specific surface area between 1 and 30 m²/g.

20

The present invention is illustrated in further detail by means of the examples described in the following:

25

Example 1:

A closed reactor as depicted in Figure 1, containing inside the

same another container with 124 g of metallic calcium among 4 kg of calcium chloride, was subjected to heating in an argon atmosphere (800 torr.) to a temperature of 900° C. After homogenization of this mixture by means of mechanical stirring, 100 g of "oxidized powder" (average particle size 2.3 microns) was added in continuous fashion. After the reduction, the mixture was cooled down to ambient temperature.

The material was removed from the reactor and subjected to dissolution in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was then filtered and rinsed with 10 liters of deionized water. The cake obtained from filtration was subsequently vacuum-dried. The chemical analysis of the obtained powder evidenced that the oxygen content had fallen from 18,000 ppm to 3,850 ppm.

15

Example 2:

A closed reactor as depicted in Figure 1, containing inside the same another container with 124 g of metallic calcium among 4 kg of calcium chloride, was subjected to heating in an argon atmosphere (800 torr.) to a temperature of 900° C. After homogenization of this mixture by means of mechanical stirring, 100 g of "oxidized powder" (average particle size 18.6 microns) was added in continuous fashion. After the reduction, the mixture was cooled down to ambient temperature.

25

The material was removed from the reactor and subjected to dissolution in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was

then filtered and rinsed with 10 liters of deionized water. The cake obtained from filtration was subsequently vacuum-dried. The chemical analysis of the obtained powder evidenced that the oxygen content had fallen from 6,300 ppm to 785 ppm.

5

Example 3:

A closed reactor as depicted in Figure 1, containing inside the same another container with 124 g of metallic calcium among 4 kg of calcium chloride, was subjected to heating in an argon atmosphere (800
10 torr.) to a temperature of 900° C. After homogenization of this mixture by means of mechanical stirring, 100 g of "oxidized powder" (average particle size 1.1 micron) was added in continuous fashion. After the reduction, the mixture was cooled down to ambient temperature.

15 The material was removed from the reactor and subjected to dissolution in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was then filtered and rinsed with 10 liters of deionized water. The cake obtained from filtration was subsequently vacuum-dried. The chemical analysis of
20 the obtained powder evidenced that the oxygen content had fallen from 52,210 ppm to 10,500 ppm (equivalent to 4,565 ppm/(m²/g)).

Example 4:

A closed reactor as depicted in Figure 1, containing inside the
25 same another container with 40 g of metallic magnesium in a mixture of 3.2 kg of calcium chloride and 0.8 kg of potassium chloride, was subjected to heating in an argon atmosphere (800 torr.) to a temperature of 900° C.

After homogenization of this mixture by means of mechanical stirring, 100 g of "oxidized powder" (average particle size 1.9 micron) was added in continuous fashion. After the reduction, the mixture was cooled down to ambient temperature.

5

The material was removed from the reactor and subjected to dissolution in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was then filtered and rinsed with 10 liters of deionized water. The cake obtained from filtration was subsequently vacuum-dried. The chemical analysis of the obtained powder evidenced that the oxygen content had fallen from 39,620 ppm to 6,700 ppm (equivalent to 4,188 ppm/(m²/g)).

10

Example 5:

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The oxidized powder (11 g) was placed on a metallic screen, attached to the support stem (11), inside a crucible 1, as shown in Figure 2. The metallic magnesium (25 g) was placed in the reducer container (Ca/Mg, NbH), also attached to the support stem (2). The mixture of calcium chloride (240 g) and potassium chloride (60 g) was placed inside the crucible, together with the oxidized powder and the metallic magnesium. The crucible was sealed, there being welded a cover thereon. The mixture was heated to a temperature of 900° C for 2 hours. After the reduction, the mixture was cooled down to ambient temperature.

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The material was removed from the crucible and dissolved in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was then filtered and

rinsed with deionized water. The cake obtained from filtration was subsequently vacuum-dried. The chemical analysis of the obtained powder evidenced that the oxygen content had fallen from 52,210 ppm to 5,850 ppm (equivalent to 3,250 ppm/(m²/g)).

5

Example 6:

The oxidized powder (11 g) was placed on a metallic screen, attached to the support stem (11), inside a crucible (1), as shown in Figure 2. The metallic calcium (25 g) was placed in the reducer container (Ca/Mg, NbH), also attached to the support stem. The calcium chloride (300 g) was placed inside the crucible, together with the oxidized powder and the metallic calcium. The crucible was sealed, there being welded a cover thereon. The mixture was heated to a temperature of 900° C for 2 hours. After the reduction, the mixture was cooled down to ambient temperature.

15

The material was removed from the crucible and dissolved in deionized water. The solid phase was leached with an aqueous solution containing HCl and HF for 90 minutes. This mixture was then filtered and rinsed with deionized water. The cake obtained from filtration was subsequently vacuum-dried. The chemical analysis of the obtained powder evidenced that the oxygen content had fallen from 52,210 ppm to 5,520 ppm (equivalent to 3,070 ppm/(m²/g)).

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The typical morphology of the powders produced using the processes set forth herein may be seen in the image of back-scattered electrons shown in Figure 3.

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CLAIMS

1. A process for the production of niobium and/or tantalum powder with large surface area, characterized by comprising the steps of reduction of the oxidized powder (powder of adequate size, consisting basically in metallic niobium and/or tantalum and/or hydrides thereof, of high purity, previously oxidized in a controlled manner) with alkali or earth alkali metals and/or metal hydrides in a bath of molten salt, or within a solution of molten salts, subsequently followed by leaching, filtration, rinsing and drying the product thus obtained.

2. A process for the production of niobium and/or tantalum powder with large surface area, according to Claim 1, characterized in that the reducing step comprises as reactive elements calcium and magnesium or another alkali metal or earth alkali metal and/or metal hydride capable of reducing the niobium and/or tantalum oxide or the oxidized compounds thereof.

3. A process for the production of niobium and/or tantalum powder with large surface area, according to Claim 1, characterized in that the bath comprises a molten salt or a mixture of molten salts comprised by chlorides or fluorides of alkali metals or earth alkali metals.

4. A process for the production of niobium and/or tantalum powder with large surface area, according to Claim 3, characterized in that the chlorides or fluorides of alkali metals or earth alkali metals comprise CaCl_2 , NaCl , MgCl_2 , KCl , CaF_2 .

5. A process for the production of niobium and/or tantalum powder with large surface area, according to Claim 1, characterized in that the reducing step comprises a salt bath at temperatures

between 300° C and 1200° C.

6. A process for the production of niobium and/or tantalum powder with large surface area, according to Claim 1, characterized in that the reduction of the oxidized metal is carried out in a salt bath under mechanical stirring or under stirring by an inert or reactive gas containing nitrogen.

7. A process for the production of niobium and/or tantalum powder with large surface area, according to Claim 1, characterized in that the oxidized powder is fed in a continuous and controlled manner to the bath of salts containing the reducing agent.

8. A process for the production of niobium and/or tantalum powder with large surface area, according to Claim 1, characterized in that the mixture of the oxidized powder and the reducing agent in the salt bath is carried out prior to the melting step.

9. A process for the production of niobium and/or tantalum powder with large surface area, according to Claim 1, characterized in that the reduction in molten salt is carried out in a controlled atmosphere with partial pressures of nitrogen that may vary between 0.0005 atm (0.506625 mbar) and 1 atm (1013.25 mbar) or by means of injection of N₂ gas or a mixture of inert gas and N₂ (containing from 0.1 to 50% N₂) in the molten salt, and by addition of nitrogen compounds to the salt bath in order that there may be obtained powders of niobium and/or tantalum with nitrogen contents varying from 100 to 70,000 ppm.

10. A process for the production of niobium and/or tantalum powder with large surface area, according to Claim 1, characterized in that the step of recovery of the niobium and/or tantalum

powder is conducted by means of the procedures of solubilization of the salt in water and leaching of the solid product obtained by using an acidic aqueous solution containing HCl and HF.

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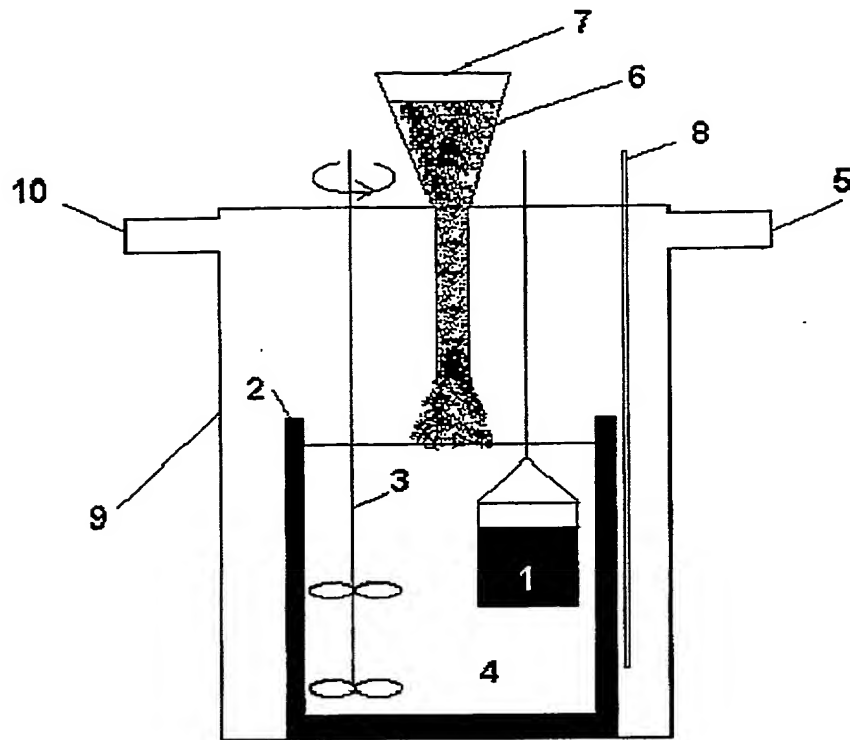


FIG. 1

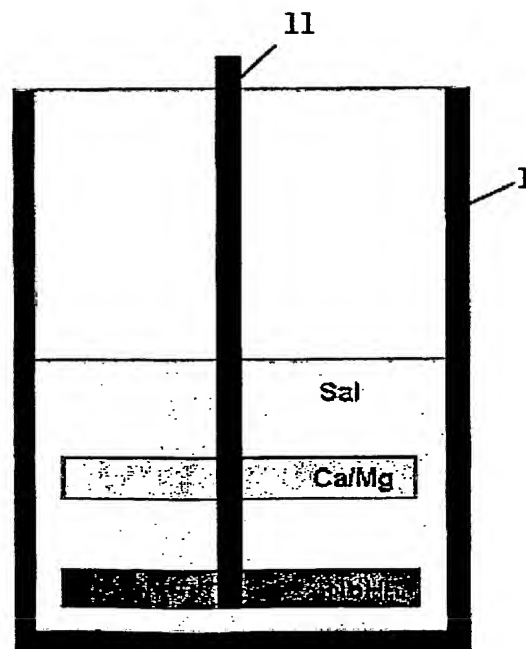


FIG. 2

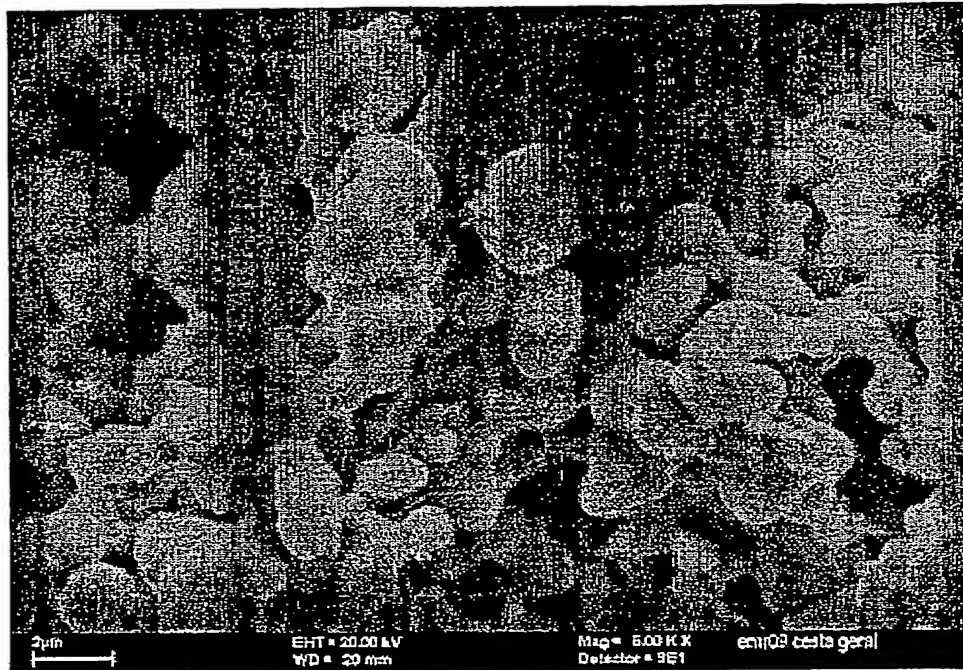


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/BR 03/00122

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B34/20 C22B5/04 B22F9/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 923 531 A (FISHER RICHARD L) 8 May 1990 (1990-05-08) column 2, line 16 - line 53; claims 1-3,5,18; examples 5,7,8	1-10
Y	US 5 234 491 A (CHANG HONGTU) 10 August 1993 (1993-08-10) column 7, line 58 -column 8, line 55	1-10
Y	US 4 487 677 A (MURPHY ANDREW H) 11 December 1984 (1984-12-11) figures 3B-3D	1-4
Y	GB 2 233 349 A (CABOT CORP) 9 January 1991 (1991-01-09) example 1	1,2,10
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- *Z* document member of the same patent family

Date of the actual completion of the international search

27 January 2004

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bombeke, M

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